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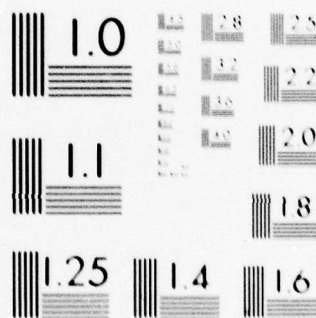
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TECHNICAL REPORT ARBRL-TR-02178

ELECTRON SPIN RESONANCE STUDIES OF
HYDROGEN AND DEUTERIUM BOMBARDMENT OF
UNSATURATED HYDROCARBONS AT 77K

Cornellius U. Morgan
Kevin J. White

July 1979



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
BALLISTIC RESEARCH LABORATORY
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TECHNICAL REPORT ARBRL-TR-02178	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER 9
4. TITLE (and Subtitle) ELECTRON SPIN RESONANCE STUDIES OF HYDROGEN AND DEUTERIUM BOMBARDMENT OF UNSATURATED HYDROCARBONS AT 77K	5. TYPE OF REPORT & PERIOD COVERED Technical Report	
7. AUTHOR(s) Cornelius U./Morgan Kevin J./White	6. PERFORMING ORG. REPORT NUMBER	
8. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Ballistic Research Laboratory ATTN: DRDAR-BLP Aberdeen Proving Ground, MD 21005	9. CONTRACT OR GRANT NUMBER(s) 12/30p	
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Armament Research and Development Command U.S. Army Ballistic Research Laboratory ATTN: DRDAR-BL Aberdeen Proving Ground, MD 21005	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1L161102AH60	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	12. DATE JUL 79	
	13. NUMBER OF PAGES 28	
	15. SECURITY CLASS. (of this report) Unclassified	
	18a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) 18 SBIE 19 AD-E430 296		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) H Atom Addition Unsaturated Hydrocarbon Electron Spin Resonance		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) jmk The interaction of free atoms and radicals with unsaturated compounds has been a field of considerable interest. In this present work, the reactions of solid unsaturated hydrocarbons at 77K with gaseous hydrogen atoms are studied by electron spin resonance (esr). The hydrogen atom adds directly to the terminal position of the double bond of trans-2-butene, 2,3-dimethyl-1,3-butadiene, 2-methyl-1-butene-3-yne, 3,3-dimethyl-1-butene, isobutylene, ethylene, and propylene to produce the sec-butyl, 2,3-dimethyl-2-butenyl,		

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20. ABSTRACT: (Continued)

21,1-dimethyl-2-propynyl, 1,2,2-trimethyl propyl, t-butyl, ethyl, and isopropyl radicals, respectively. The addition reaction of H atoms to trans-1,3-pentadiene occurs at the terminal carbon atom of the terminal double bond to produce the 1-methyl-2-butenyl radical. Confirmation of an addition reaction was made by bombarding the unsaturate first with hydrogen and then with deuterium. The two radicals can be distinguished by their esr spectra. On bombardment of allene with H atoms the allenyl radical was observed. This radical was produced by an abstraction of a hydrogen atom from allene.

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I. INTRODUCTION

The goal of a number of research programs has been the development of a more energetic propellant. Examples of some of this work are given in references 1 and 2. The stabilization of very reactive species such as radicals in conventional propellants was one of the methods used.

In the development of an energetic propellant the inability to attain a substantial concentration of radicals in the propellant is one of the primary obstacles to making a significant contribution to the total energy of the system. Calculations have been made on particular systems^{3,4} but the actual parameters required for producing high concentrations of radicals are not well understood. Some methods that have been used to produce free radicals in solids are high energy radiation, photolysis, and generation of free radicals in the gas phase with a microwave discharge followed by condensation and trapping of produced radicals at low temperature. All of these techniques have some deficiencies. With bond scission by radiation the fragments produced must migrate far enough from each other in the solid to prevent recombination. With the discharge and condensation method considerable reaction takes place when the radicals collide with the substrate. The mechanisms of trapping radicals within matrices is a field that is not well understood. Pimentel (see reference 1, chapter 4) has established a general rule on the macroscopic level which states that radical species cannot be preserved if the temperature of the matrix substance is higher than approximately $T_m/2$, where T_m is the melting point of the matrix.

The mechanisms of radical trapping of hydrogen atoms in various matrices have been published by Ultee and Kepford⁵. A study by one of the present authors⁶ on the trapping of methyl radicals has also been completed. Both of these papers are directed at a better understanding

1. A. M. Bass and H. P. Broida, Formation and Trapping of Free Radicals, Academic Press, New York, NY, 1960.
2. G. C. Szego, "Free Radical Fuels", Chem. Eng. Progr., 56, 60-63 (1960).
3. J. L. Jackson and E. W. Montroll, "Free Radical Statistics", J. Chem. Phys., 28, 1101-9 (1958).
4. J. L. Jackson, "Dynamic Stability of Frozen Radicals. I. Description and Application of the Model", J. Chem. Phys., 31, 154-7 (1959).
5. C. J. Ultee, and C. Kepford, "Study of Stabilization of Hydrogen Atoms at 77 K and Higher Temperatures", AFRPL-TR-68-73, (1968).
6. C. U. Morgan, "Decay Kinetics of the Methyl Radical Produced by Ultra-Violet Irradiation of Methanol-Water Matrices at 77 K", Ballistic Research Laboratory, Aberdeen Proving Ground, MD, BRL Report No. 1422, October 1968 (AD #678563).

of the mechanisms involved in radical trapping in matrices. One objective of this task is to investigate the technique of trapping radicals produced by the interaction of active species such as hydrogen atoms with unsaturated compounds at 77K. Radicals that are formed by this method are not fragmented species and do not require the migration of species to prevent recombination as in the case of the photolytic or radiolytic techniques. This method also avoids the unwanted reactions that take place when radicals are condensed from the gas phase. The problem of how the reactivity of the radicals affects the stability of the matrix should also be considered.

Klein and others⁷⁻¹³ for a number of years investigated the reaction of H atoms with unsaturated hydrocarbons primarily by the analysis of the products when they had warmed to room temperature. An objective of this work was to investigate directly the radicals produced in these reactions by using electron spin resonance (esr).

Several authors^{14,15} have postulated the importance of surface reactions in relation to unstable ignition and combustion phenomena but detailed knowledge concerning information on the reaction of gas phase products with condensed reactants is inadequate. A second objective of

7. R. Klein, M. D. Scheer, and R. Kelley, "Disproportionation-Combination Reactions of Alkyl Radicals and Hydrogen Atoms at Low Temperature", *J. Phys. Chem.*, 68, 598-605 (1964).
8. R. Klein, and M. D. Scheer, "Matrix Effects in the Gaseous H Atom-Condensed Olefin System; Surface Reaction--Olefin Diffusion Model", *J. Phys. Chem.*, 66, 2677-81 (1962).
9. R. Klein and M. D. Scheer, "The Activation Energy for Hydrogen Addition to Propylene", *J. Phys. Chem.*, 65, 375-77 (1961).
10. R. Klein, M. D. Scheer, and J. G. Waller, "The Reaction of Hydrogen Atoms with Solid Propene at Low Temperatures", *J. Phys. Chem.*, 64, 1247-50 (1960).
11. R. Klein and M. D. Scheer, "The Addition of Hydrogen Atoms to Solid Olefins at -195°", *J. Am. Chem. Soc.*, 80, 1007 (1958).
12. R. Klein and M. D. Scheer, "Cross Dimerization in the Hydrogen Atom Addition to Mixtures of Solid Olefins at 77 K", *Preprint Papers, International Symp. Free Radicals*, 5th, Upsala 34-2-5 (1961).
13. R. Klein and M. D. Scheer, "The Reaction of Hydrogen Atoms with Solid Olefins at -195°", *J. Phys. Chem.*, 62, 1011-1014 (1958).
14. F. E. C. Culick, "Some Problems in the Unsteady Burning of Solid Propellants", NWC Tech. Pub. 4668, (1969).
15. R. S. Brown and R. J. Muzzy, "Research on Combustion of Solid Propellants", UTC Report No. 2136-TSR2, (1967).

this investigation is to illuminate some of the basic reactions of hydrogen atoms with unsaturated compounds. These experiments compliment those of Klein and others. Other authors who have contributed to this field are Bazhin, Kuznetsov, Bubnov, and Voevodzkii¹⁶ with their work on the addition of H atoms to ethylene and acetylene in low temperature acid matrices to produce the ethyl and vinyl radicals. Hill, Reid, and Strandberg¹⁷, in studying the bombardment of a propylene film with hydrogen atoms, calculated the kinetic rate constant for the reaction $H + H_2C=CH-CH_3 \rightarrow CH_3\dot{C}HCH_3$. When Cochran, Adrian, and Bowers¹⁸ photolyzed HI in acetylene at 4.2 K, the hydrogen atoms produced added to the triple bonds of acetylene to form vinyl radicals. Similarly, Aditya and Willard¹⁹ photolyzed matrices of HI, 3-methyl pentane, and various alkanes or alkenes at 77 K to produce radicals. Forchioni and Chachaty²⁰ bombarded various organic compounds at 77 K with active nitrogen to produce radicals. Chachaty and Schmidt²¹ bombarded methyl methacrylate, vinyl acetate, acrylonitrile, methyl acrylonitrile, and styrene with H atoms to produce radicals. These radicals were formed by addition to the double bond at the terminal position. Abstractive radicals were obtained when allyl alcohol, ethanol, isopropanol, and 2-chloroethanol were bombarded with H atoms. Others²²⁻²⁴ have produced radicals in polymers or solids by

16. N. M. Bazhin, E. V. Kuznetsov, N. N. Bubnov, and V. V. Voevodzkii, "Hydrogen Atom Reactions in a System $H_2O + H_2SO_4 + FeSO_4$. II. Reactions with Unsaturated Compounds", *Kinekika i kataliz*, 7, 161-5 (1966).
17. C. C. Hill, Jr., R. C. Reid, and M. W. D. Strandberg, "Reactions of Atomic Hydrogen with Propylene at 77 K as Studied by Electron Spin Resonance", *J. Chem. Phys.*, 42, 4170-74 (1965).
18. E. L. Cochran, F. J. Adrian, and V. A. Bowers, "E.S.R. Study of Ethynyl and Vinyl Free Radicals", *J. Chem. Phys.*, 40, 213-20 (1964).
19. S. Aditya and J. Willard, "Radical Formation by the Photolysis of Hydrogen Iodide at 77 K in Alkane-Alkene, and Alkene Matrices", *J. Am. Chem. Soc.*, 88, 229-32 (1966).
20. A. Forchioni and C. Chachaty, "Free Radicals Formed by the Reaction of Active Nitrogen on Organic Compounds at 77 K", *Comptes Rendus*, 264, 637-40 (1967).
21. C. Chachaty and M. C. Schmidt, "Free Radicals Formed by the Reaction of Gas Phase Hydrogen Atoms on Various Organic Compounds at 77 K", *J. Chim. Phys.*, 62, 527-35 (1965).
22. L. A. Wall and R. B. Ingalls, "Reactions of Deuterated Polystyrenes with Hydrogen and Deuterium Atoms", *J. Chem. Phys.*, 41, 1112-20 (1964).
23. T. Cole and H. C. Heller, "Production of Free Radicals in Organic Solids by Hydrogen-Atom Bombardment", *J. Chem. Phys.*, 42, 1668 (1965).
24. J. N. Herak and W. Gordy, "Interaction of Hydrogen Atoms and Hydroxyl Radicals with 5-Halogen Uracils", *Proceedings of the National Academy of Sciences*, 56, 1354-60 (1966).

bombarding with H or D atoms at room temperature. In an earlier report²⁵ ethylene, propyne, 1,3-butadiene, 1-butyne, 1,2-butadiene, 1,4-cyclohexadiene, and benzene were bombarded with H atoms to produce, respectively, the ethyl, allenyl, 2-butenyl, methylallenyl, methylallenyl, cyclohexadienyl, and cyclohexadienyl radicals. In more recent work by Bennett and Mile²⁶ radicals were produced by H atom bombardment of unsaturated compounds in an inert matrix. This was accomplished by bombarding a steel drum rotating cryostat cooled to 77K alternately with streams of argon, unsaturated hydrocarbon, and then H atoms.

II. EXPERIMENTAL

The gases used in the work included Matheson trans-2-butene (99.0%), isobutylene (99.0%), hydrogen (99.9%), deuterium (98.0%), allene (97%), ethylene (99.5%), and butane (99.0%). The liquid samples used were furnished by the Chemical Samples Company. They were trans-1,3-pentadiene (99%), 2,3-dimethyl-1,3-butadiene (99%), 3,3-dimethyl-1-butene (99.9%), and 2-methyl-1-butene-3-yne (99%). These were not purified further. The experimental apparatus and conditions were the same as those described in a previous publication²⁵ with the exception that a Varian V-4535 Large Sample Access cavity was used in the esr system.

Essentially, the system consisted of a glass flow tube in which hydrogen or deuterium gas was passed through a microwave discharge or a hot tungsten filament²⁷ to produce the free atoms. The atoms then bombarded the sample held on a cold finger at 77 K located in an esr cavity.

Computer simulation of the experimentally obtained spectra was carried out for most of the cases examined.

25. C. U. Morgan and K. J. White, "The Electron Spin Resonance Spectra of Radicals Produced by the Hydrogen and Deuterium Bombardment of Unsaturated Organic Compounds at 77 K", Ballistic Research Laboratory, Aberdeen Proving Ground, MD, BRL Report No. 1453, October 1969, AD #697728.
26. J. E. Bennett and B. Mile, "Studies of Radical-Molecule Reactions Using a Rotating Cryostat", *J.C.S. Faraday, I*, **69**, 1398 (1973).
27. K. J. White, C. U. Morgan, and E. Freedman, "A Simple Technique for Generating Nitrogen Atoms", Ballistic Research Laboratory, Aberdeen Proving Ground, MD, BRL Memorandum Report No. 2168, March 1972, AD #739520.

III. RESULTS AND DISCUSSION

A. Trans-2-butene

Trans-2-butene was bombarded with hydrogen atoms and the spectrum of the radical produced is shown in Figure 1A.

The addition of a H atom to the double bond of trans-2-butene can produce only the sec-butyl radical. Asycough and Thomson²⁸ showed that the two beta protons of the methylene group in radicals like the sec-butyl are not equivalent. They concluded that these protons were about 15° away from the symmetrical arrangement of the two protons above and below the plane perpendicular to the the unpaired electron. Such a configuration would yield roughly five equivalent protons (1a and 4b). The other β proton gives a coupling constant approximately twice as large as the equivalent protons. The observed spectrum can be explained by assuming the following hyperfine splitting constants:

$$a_{\alpha H} = a_{\beta_1 H} = a_{MeH} = 2.3 \pm 0.1 \text{ mT}$$

$$a_{\beta_2 H} = 4.4 \pm 0.1 \text{ mT}$$

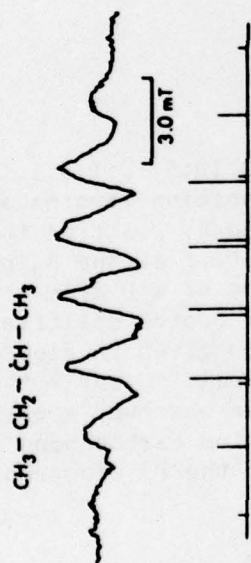
and an intensity distribution of 1:5:1:10:5:10:10:5:10:1:5:1. For the deuterium bombardment of trans-2-butene the question remains as to the β position of the deuterium. If it adds to the β_1 position then the deuterium splitting would be about 0.35 mT, but if at the β_2 position the splitting would be about 0.68 mT. Addition of a D atom at the β_2 position would also eliminate the large 4.4 mT proton splitting. The stick diagrams of both these configurations are given in Figure 1B under the spectrum for the deuterated sec-butyl radical. Clearly the deuterium in β_1 or small splitting configuration fits the observed spectrum. The small splitting position means that the deuterium carbon bond makes an angle of approximately 135° with the z axis of the P_z electron.

B. 2,3-dimethyl-1,3-butadiene

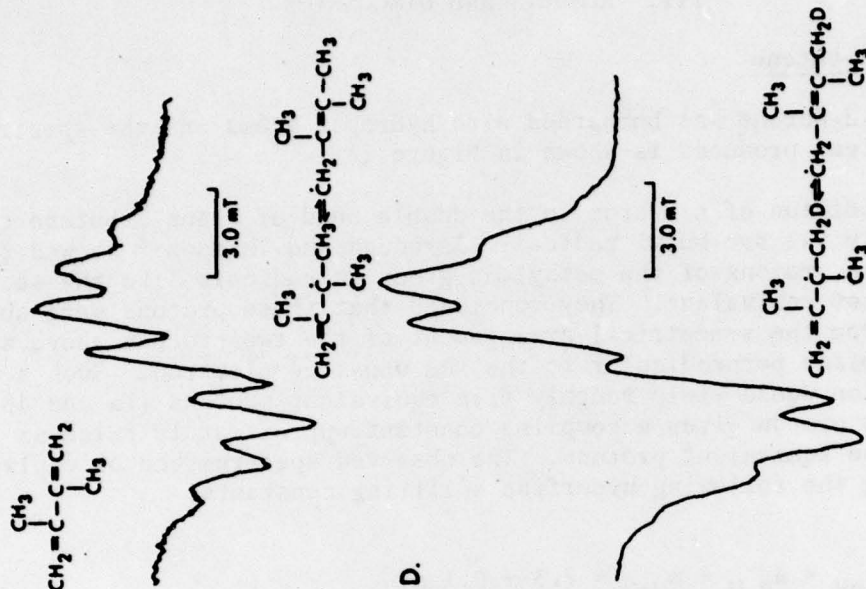
Bombardment of 2,3-dimethyl-1,3-butadiene with hydrogen atoms yields the spectrum shown in Figure 1C. The spectrum consists of seven equally spaced lines with an isotropic splitting constant of 1.46 mT. When the spectrum was scanned at a higher gain, two wing lines appeared revealing

28. P. B. Asycough and C. Thomson, "Electron Spin Resonance Spectra of Alkyl Radicals in Gamma-Irradiated Alkyl Halides", Trans. Faraday Soc., 58, 1477 (1962).

A. TRANS-2-BUTENE
 $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$



C. 2,3-DIMETHYL-1,3-BUTADIENE



D.

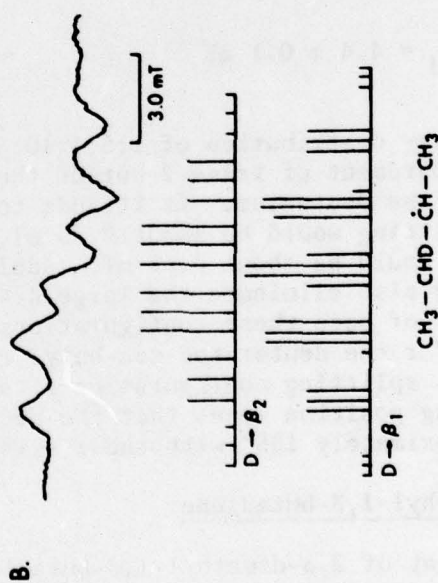


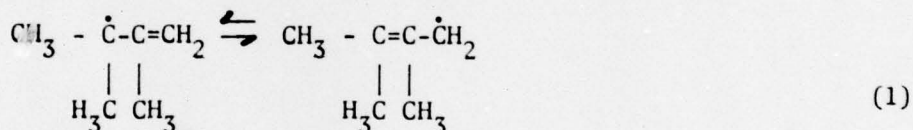
Figure 1A. Spectrum and intensity stick diagram of sec-butyl radical.
 B. Spectrum of the singly deuterated sec-butyl radical ($\text{CH}_3\text{CHDCH}_2\text{CH}_3$) and intensity diagrams of two possible configurations.
 C. Spectrum of the 2,3-dimethyl-2-butenyl radical.
 D. Spectrum of the single deuterated 2,3-dimethyl-2-butenyl radical. All spectra recorded at 77K.

a nine line spectrum instead of seven. The displacement of the spectrum about the base line indicates that a broad single line resonance is superimposed on top of the nine line spectrum.

To assist in the analysis, the 2,3-dimethyl-1,3-butadiene was bombarded with D atoms and a spectrum of 8 lines was produced as shown in Figure 1D.

The splitting due to deuterium is approximately 1/6 that due to hydrogen and consequently contributes mainly a broadening effect to the remaining hyperfine lines of the spectrum. Thus, the spectrum produced by deuterium addition always contained one less line than that produced by hydrogen addition. The deuterium spectrum in the above case confirms the addition mechanism since an abstraction by H or D would yield the same spectrum.

The addition of H atoms to 2,3-dimethyl-1,3-butadiene at the terminal position would give radical (1), 1,1,2-trimethylallyl, whose resonance hybrid is 2,3-dimethyl-2-butenyl.



If the proton adds to the second position we get radical (2), 2,3-dimethyl-3-butenyl.



Radical (1) has eight equivalent protons (2 α and 6 β) interacting with the unpaired electron and should produce a nine line spectrum with intensity distribution 1:8:28:56:70:56:28:8:1. Radical (2) on the other hand has only three interacting protons and could not yield the observed spectrum. The spectrum is accounted for by radical (1) plus a broad underlying unknown resonance.

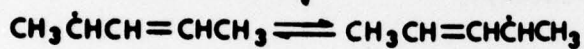
C. Trans-1,3-Pentadiene

Trans-1,3-pentadiene was bombarded with hydrogen atoms and the radical produced gave the esr spectrum shown in Figure 2A. Seven equally spaced lines are observed with an isotropic splitting constant of 1.55 mT. In the case of an addition reaction the hydrogen atom could add at the 1,2,3, or 4 position in trans-1,3-pentadiene. Radicals (3), (4), (5), or (6) could be produced.

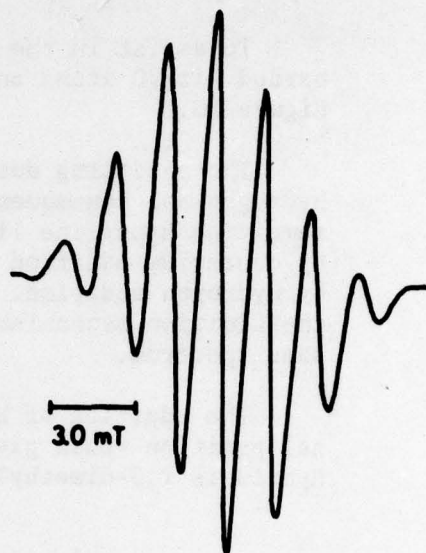
A. TRANS-1, 3-PENTADIENE



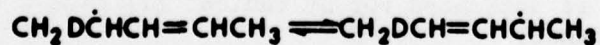
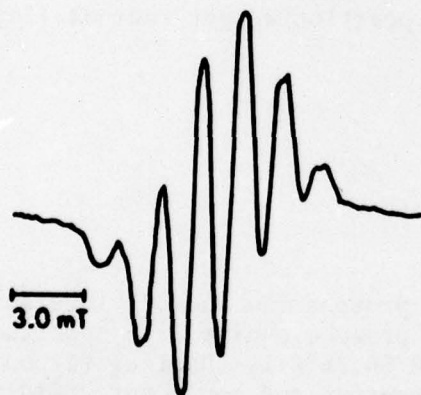
3.0 mT



B.



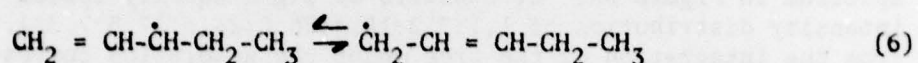
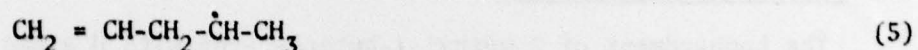
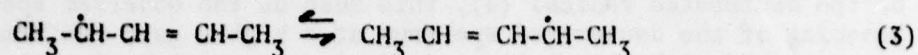
C.



D.



Figure 2A. Spectrum of the 1-methyl-2-butenyl radical.
 B. Computer simulated spectrum of the 1-methyl-2-butenyl radical.
 C. Spectrum of the singly deuterated 1-methyl-2-butenyl radical.
 D. Spectrum of the single deuterated 1-methyl-2-butenyl radical at high gain. All spectra recorded at 77K.



Radical (3), 1-methyl-2-butenyl, has eight equivalent protons (2 α and 6 β) interacting with the free electron. This radical would produce a nine line spectrum with an intensity distribution of 1:8:28:56:70:56:28:8:1. Computer simulation of the observed spectrum clearly shows that the seven lines have an intensity distribution of the middle seven lines of the spectrum for radical (3). Computer simulation also indicates that the two wing lines would be buried in the noise (Figure 2B). Radical (4), 3-pentenyl, has 3 equivalent (2 α and 1 β) and one inequivalent β protons interacting with the free electron. This would produce a six line spectrum with an intensity distribution of 1:3:4:4:3:1. The methylene group protons in this type of unsaturated radical²⁹ exhibit the same steric characteristics as in the saturated radicals. Radical (5), 1-methyl-3-butenyl, has five equivalent (1 α and 4 β) and one inequivalent β protons interacting with the free electron and would produce an eight line spectrum with an intensity distribution of 1:5:11:15:15:11:5:1. Radical (6), 2-pentenyl, has four equivalent (3 α and 1 β) and one inequivalent β protons interacting with the free electron. This would yield a seven line spectrum with intensity distribution of 1:4:7:8:7:4:1. Clearly radicals (4) and (5) can be eliminated from consideration as the species that produces the spectrum but radicals (3) and (6) are still possibilities.

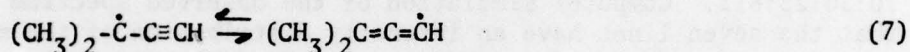
To assist in the analysis the trans-1,3-pentadiene was bombarded with D atoms and the resulting spectrum is shown in Figure 2C. If the deuterium adds to the double bond as H does in radical (6) in such a way that the proton remaining in the methylene group is inequivalent to the other protons, then a spectrum of six lines with intensity distribution of 1:3:4:4:3:1 would be generated. If it adds so as to make all remaining protons equivalent then a spectrum of five lines would result with an intensity distribution of 1:4:6:4:1. If radical (3) is the observed radical, then the intensity distribution for the spectrum of the deuterated radical would be 1:7:21:35:35:21:7:1. Since

29. P. B. Ayscough and H. E. Evans, "Electron Spin Resonance Studies of Gamma-Irradiated Olefins and u.v.-Irradiated methyl Iodide + Olefin Glasses," *Trans. Faraday Soc.*, **60**, 801 (1964).

the deuterated radical spectral intensities do not fit either case of the deuterated radical (6), but agree well with the six central lines of the deuterated radical (3), this must be the observed species. Scanning of the deuterated spectrum at a higher gain confirmed that the spectrum had eight lines instead of six as two weak wing lines were observed (Figure 2D). Only the extreme low field and high field lines are shown in Figure 2D.

D. 2-methyl-1-butene-3-yne

The bombardment of 2-methyl-1-butene-3-yne with H atoms yields the spectrum in Figure 3A. It consists of eight equally spaced lines with intensity distribution of 1.1:7.2:18.4:26.5:24.6:17.3:7.3:1.2 derived from the integration of the area under the absorption curves. The isotropic splitting constant for this radical is 1.77 ± 0.05 mT. This spectrum is produced by radical (7), 1,1-dimethyl-2-propynyl, by a terminal addition to the double bond.



The theoretical intensity distribution for this radical is 1:7:21:35:35:21:7:1. The spectrum is produced by the interaction of seven equivalent (1 α and 6 β) protons with the unpaired electron.

E. Allene

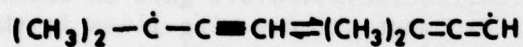
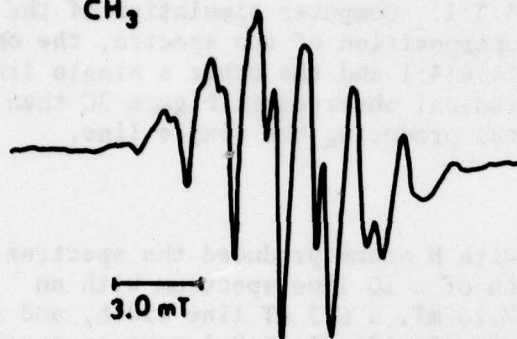
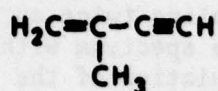
The bombardment of allene with hydrogen atoms produced the spectrum shown in Figure 3B. The peak to peak separation of the four lines are 1.80, 1.44, and 1.80 ± 0.05 mT. This species is identical to that found for the hydrogen atom bombardment of propyne²⁵ and ultraviolet irradiation of allene by Volman, Maas, and Wolstenholme³⁰. The radical producing this spectrum was identified as the allenyl radical. Hydrogen hyperfine coupling constants of 1.8 mT for the methylene group and 1.4 mT for the CH group were observed for this radical. These mechanisms are described in detail in the previous report²⁵.

F. 3,3-Dimethyl-1-butene

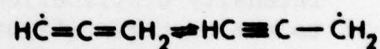
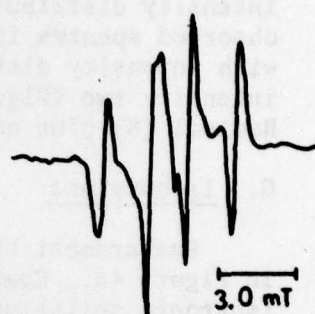
Bombardment of 3,3-dimethyl-1-butene with hydrogen atoms yields the five line spectrum shown in Figure 3C. This spectrum has an isotropic splitting constant of 2.23 mT and an intensity distribution of 1:4:8:4:1. Two possible radicals that could be produced by an addition reaction are radicals (8) and (9).

30. D. H. Volman, K. A. Maas, and J. Wolstenholme, "Photochemical Formation of Free Radicals from Olefinic and Acetylenic Compounds in the Frozen State as Studied by Electron Spin Resonance," *J. Am. Chem. Soc.* **87**, 3041 (1965).

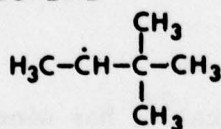
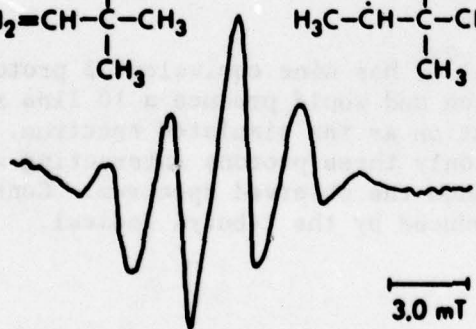
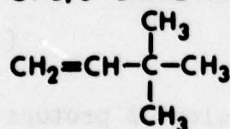
A. 2-METHYL-1-BUTENE-3-YNE



B. ALLENE



C. 3,3-DIMETHYL-1-BUTENE



D. 3,3-DIMETHYL-1-BUTENE

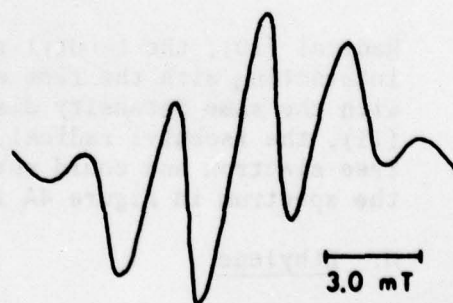


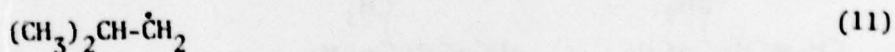
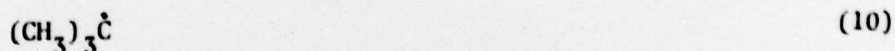
Figure 3A. Spectrum of the 1,1-dimethyl-2-propynyl radical.
 B. Spectrum of the allenyl radical.
 C. Spectrum of the 1,2,2-trimethyl propyl radical.
 D. Computer simulated spectrum of the 1,2,2-trimethyl propyl radical. All spectra recorded at 77K.



Radical (8), 1,2,2-trimethyl propyl, is produced by a terminal addition and has four equivalent (1 α and 3 β) protons interacting with the free electron. This gives a five line spectrum with an intensity distribution of 1:4:6:4:1. Radical (9), 3,3-dimethyl butyl, has three equivalent protons (2 α and 1 β) and a fourth β proton with a coupling twice as large as the others. Such a radical would yield a six line spectrum with an intensity distribution of 1:3:4:4:3:1. Computer simulation of the observed spectra indicates the superposition of two spectra, the one with intensity distribution of 1:4:6:4:1 and the other a single line of intensity two (Figure 3D). The radical observed in Figure 3C then is Radical (8) plus an unknown radical producing the single line.

G. Isobutylene

Bombardment of isobutylene with H atoms produced the spectrum shown in Figure 4A. Computer simulation of a 10 line spectrum with an isotropic splitting constant of 2.26 mT, a 0.3 mT line width, and an intensity distribution of 1:9:36:84:126:126:84:36:9:1 gave an excellent fit to the spectrum (Figure 4B). The two most extreme wing lines in the spectrum of Figure 4A were not observed. Possible radicals formed by the addition are radicals (10) and (11).

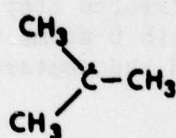
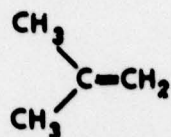


Radical (10), the t-butyl radical²⁸, has nine equivalent β protons interacting with the free electron and would produce a 10 line spectrum with the same intensity distribution as the simulated spectrum. Radical (11), the isobutyl radical, has only three protons interacting with the free electron and could not produce the observed spectrum. Consequently, the spectrum in Figure 4A is produced by the t-butyl radical.

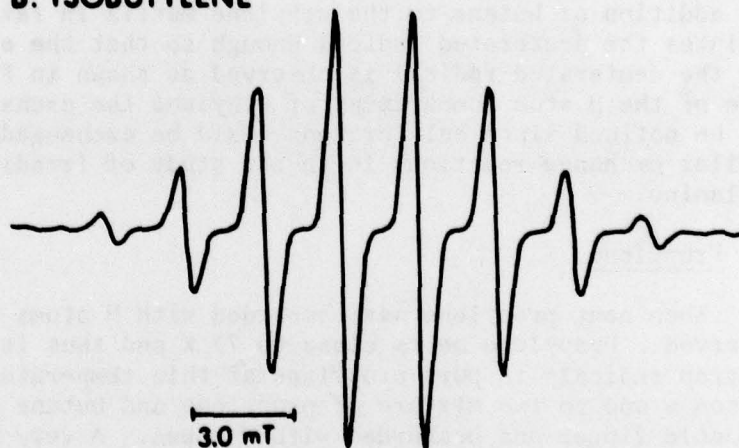
H. Ethylene

In the previous report²⁵ ethylene was bombarded with H atoms to produce the ethyl radical. In this present work neat ethylene was bombarded with D atoms and the ethyl radical was again observed. When a matrix of one third ethylene plus two thirds butane was bombarded with D atoms the spectrum produced is shown in Figure 4C. The spectrum was

A. ISOBUTYLENE



B. ISOBUTYLENE



C. ETHYLENE

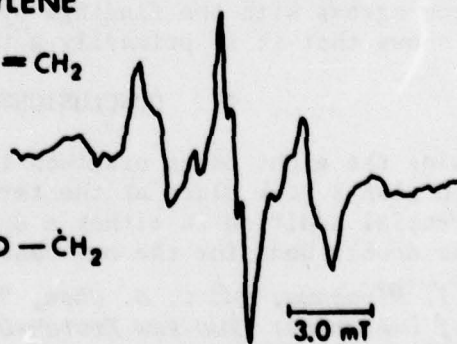
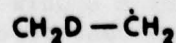
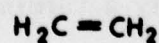


Figure 4A. Spectrum of the t-butyl radical.
 B. Computer simulated spectrum of the t-butyl radical.
 C. Spectrum and intensity stick diagram of the singly deuterated ethyl radical. All spectra recorded at 77K.

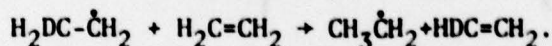
generated by the $\dot{\text{C}}\text{H}_2\text{CH}_2\text{D}$ radical and the intensity stick diagram was prepared from the hyperfine splitting constants shown below.

$$a_{\text{H}_\alpha} = 2.1 \pm 0.1 \text{ mT}$$

$$a_{\text{H}_\beta} = 2.7 \pm 0.1 \text{ mT}$$

$$a_{\text{D}_\beta} = 0.4 \pm 0.1 \text{ mT}$$

The failure to observe the singly deuterated ethyl radical in the case of the bombardment of neat ethylene with D atoms was probably due to an exchange reaction between ethylene and the deuterated radical:



The addition of butane to the ethylene matrix in ratio of two to one isolates the deuterated radical enough so that the exchange is decreased and the deuterated radical is observed as shown in Figure 4C. In the case of the H atom bombardment of ethylene the exchange reaction would not be noticed since only protons could be exchanged. Itoh³¹ observed similar exchange reactions in an esr study of irradiated crystals of L-alanine.

I. Propylene

When neat propylene was bombarded with H atoms no resonance was observed. Propylene melts close to 77 K and thus it may be impossible to trap radicals in pure propylene at this temperature. For this reason a one to two mixture of propylene and butane was condensed on the cold finger and bombarded with H atoms. A very weak and poor quality spectrum of the isopropyl radical was observed. Only the six central lines of the eight line spectrum were observed. The observation of this spectrum agrees with the findings of Bennett and Mile²⁶ for propylene and shows that it is primarily a terminal addition.

IV. CONCLUSIONS

In reviewing the eight cases examined in which H atoms add to double bonds, addition always took place at the terminal position. In the case of preferential addition to either a double or triple bond, addition occurred at the double bond for the one case observed, the bombardment

31. K. Itoh, I. Miyagawa, and C. S. Chen, "ESR Study of an Irradiated Crystal of L-Alanine: Two New Proton-Deuteron Exchange Reactions," *J. Chem. Phys.* **52**, 1822 (1970).

of 2-methyl-1-butene-3-yne. Pimentel's general rule concerning the temperature of the matrix necessary to trap radical species did not hold in the case of ethylene. Ethylene trapped ethyl radicals at 77 K, only 26 degrees below its melting point. Although the radicals were trapped at 77 K in ethylene, an atom exchange reaction between the radical and matrix did take place.

In the case of allene, a very reactive intermediate addition radical is first formed but has a short lifetime at 77K. This result is important in connection with the mechanism of stabilizing radicals in matrices. It clearly demonstrates the fact that the stabilization of energetic species depends strongly on its reactivity and not exclusively on the melting point of the matrix.

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